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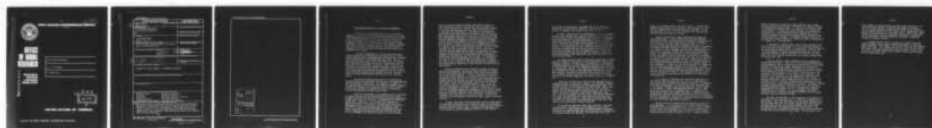
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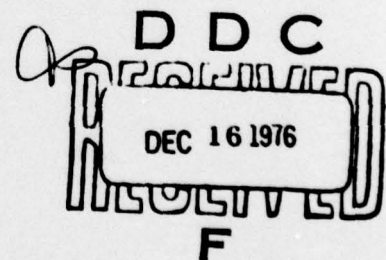
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SOLID-VACUUM INTERFACES

Dr. T.A. KITCHENS

7 OCTOBER 1976



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report briefly recounts the highlights of the Fourth International Symposium on Surface Physics held at the Eindhoven University of Technology on 23-25 June 1976. The emphasis of the meeting was on Solid-Vacuum interfaces. Six invited papers were given, most of which were discussions of recent advances in understanding the analytical techniques used in surface science.		

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SOLID-VACUUM INTERFACES - A SYMPOSIUM IN EINDHOVEN

The week of 21 June 1976 was surface-science week in Eindhoven. On the first two days the Arbeitsgemeinschaft Vakuum (Vacuum working group) of the Deutsche Physikalische Gesellschaft held a meeting--auf Deutsch--with eight sessions held two at a time. The papers were grouped into sessions on absorption, electronic properties of clean surfaces, semiconductor surfaces, reactions on surfaces, electron emission, ion exchange and methods. Since this was a national meeting, the papers were not reviewed, and several of them were concerned with matters well outside of these topics.

I arrived in Eindhoven in time for the Fourth International Symposium on Surface Physics, organized by the Nederlandse Vacuumvereniging (The Netherlands Vacuum Society, or NEVAC) and held biannually in the Netherlands since 1970. Here the papers were reviewed, and in fact, only 40% of the 112 received were presented, which meant that only 13 sessions were held of which four (two by two) were in parallel. Most of the 220 participants were from northern Europe or England, though 10% were from France, and Switzerland was well represented. Half of the six invited papers were presented by Americans, perhaps illustrating the relative strength of the subject in the US. Interestingly, the total North American representation was only about eight.

The town of Eindhoven owes much of its existence to applied physics, being the home of NV Philips' Gloeilampenfabrieken and their research laboratories. The emphasis on science is well demonstrated by the unusual science museum, EVOLUON, described in ESN a few years ago (E.A. Edelsack, ESN 26-11:315), and the large modern buildings of Eindhoven University of Technology in which the meetings were held on 23-25 June.

Since the Proceedings of the Symposium will be published in *Surface Science*, only a few highlights will be given here. No papers were given by the staff of Philips Research Laboratories, though several were in attendance. Nevertheless, the conference started with a Phillips. J.C. Phillips (Bell Laboratories, Murray Hill) spoke on the atomic structure and properties of semiconductors and, in particular, the experiments and developing theory in ultraviolet photoemission spectroscopy (UPS). Some of the difficulties are the effects of secondary emission and the computational problems which arise from the fact that in Si, for example, the electronic states in the third atomic

layer are still distinctly different from those in bulk Si. Phillips pointed out that, in principle, the calculations are easy if the atomic-orbital approach (the Extended Hückel method) is used and that the physics of this method is qualitatively in agreement with observations. Phillips and co-workers have begun such calculations following an approach given by Evan Kane (Bell Laboratories, Murray Hill) which will account for the primary and secondary emissions. He presented some generalizations from the approach and emphasized that the oscillator strengths, on which the emissions depend, can not be assumed to be independent of energy. In fact, the oscillator strengths depend on the square of the chemical binding and are therefore quite small for dangling bonds on the semiconductor surface. This is in good agreement with the experimental insensitivity to such bonds. Phillips then discussed reconstruction, the dependence of semiconductor surface properties on thermal history, some particular examples of chemisorption, and the angle-resolved ultraviolet photoemission spectroscopy (A-R UPS) of these. He expressed the opinion that, with the equipment now available, it is possible in a day or two to collect enough high quality data to require more than a year of analysis. He also described H.D. Hagstrum's (Bell Laboratories, Murray Hill) unique work on ion-neutralization spectroscopy.

Phillip's presentation was followed by several interesting papers on photoemission, low energy electron diffraction (LEED), and electron energy loss spectroscopy (ELS), mainly from Germany, France, Holland and Britain. G. Allan (Laboratoire de Physique des Solids, Lille) argued for a new mechanism for the (2x1) reconstruction of the silicon (111) surface. By adding intraorbital Coulomb interactions between the dangling bonds, a Hubbard-type Hamiltonian, with a half-filled band, obtains and the criterion of stability leads to the antiferromagnetic state. Since the (111) silicon surface is hexagonal, the only possible antiferromagnetic arrangement is the (2x1) structure. Allan went on to consider the Hubbard-Hamiltonian parameters with and without screening. B. Feuerbacher (European Space Research and Technology Center, Noordwijk, Holland) reported on his A-R UPS work on chemisorbed hydrogen on the (100) face of a W single crystal. His data are consistent with the hydrogen reacting with only a subset of surfaced orbitals.

Phillips' point about the relative data collection and analysis time was well illustrated by N.V. Richardson (Univ. of Birmingham) who has studied A-R UPS of several faces of palladium single crystals using HeI and NeI incident light. He showed the high sensitivity of the results to partial pressures as low as  $2 \times 10^{-9}$  torr of



inert gases, CO and benzene. Richardson has not yet begun the analysis but pointed out the importance of including the polarization as a parameter when dealing with single crystals.

W. Mönch (Laboratorium für Festkörperphysik der G.H. Duisburg, Duisberg, West Germany) gave a nicely illustrated invited talk on the correlation between the geometrical structure and the electronic states and properties on clean semiconductor surfaces. Especially interesting were the reversible superstructure transitions that occur at about 38% of the bulk melting temperature on cleaved surfaces of Si and Ge and n-type III-V compounds--but not on the p-type analogs. He reviewed what is known about the reconstructed surfaces and the models that have been put forward to correlate one or more of the properties with the geometrical order. But since these models have not yet been checked by a complete analysis of the energy-dependent LEED intensities, Mönch did not express much faith in any of them.

T.E. Madey (National Bureau of Standards, Washington) reviewed desorption methods, especially as used to investigate kinetics and bonding at surfaces. In particular, he emphasized the temperature-programmed desorption or flash desorption, pioneered by G. Ehrlich (U. Of Illinois), and electron stimulated desorption (ESD) as probes of chemisorption bonding. I was especially impressed with the technical resolutions of some of the experimental difficulties in the ESD technique. The major difficulties arise from the fact that for incidence energies near 100 eV only one electron out of every million or even billion bombarding the surface results in a detached ion.

Madey and co-workers have found that the desorbed ions are sometimes emitted at well-defined angles. This phenomenon contains information about the symmetries of the binding forces and is especially sensitive to the existence of surface steps. Madey illustrated these effects for several systems, but one of the most dramatic was SF<sub>6</sub> physisorbed on oxygen adsorbed on the (110) surface of W which has monatomic layer surface steps about every 50 Å. The results suggest that the sites of the SF<sub>6</sub> are associated with steps up to about 500 K but that above 500 K and SF<sub>6</sub> sites are simply six-fold symmetric. Auger Electron Spectroscopy (AES) studies of the underlying oxygen indicates that O ions are at the steps while O<sub>2</sub> and neutral O reside elsewhere.

Of the several desorption papers that followed, I felt that the most elegant, probably due to its simplicity, was the work reported by R. Jaeger (Technische Universität München, Garching). This work correlated ESD, TPD, LEED, and work-function investigations to determine a model for hydrogen on the (100) face of W. The

result is a two-state model; the initial state, *i*, has four-fold symmetry and saturates at 1/4 coverage. The final state, *f*, has two-fold symmetry and a 1000-fold decrease in the ESD. As the coverage moves from 1/4 to 1, the *i*-states become progressively unfilled and the *f*-states more filled.

Several calculations of LEED intensities were among the contributed papers. K. Heinz (Universität Erlangen-Nürnberg) explained his T-matrix approximation calculations as applied to the (100) surface of Pt, both clean and with different coverages of Cs, for incident electron energies between 15-500 eV. C. G. Kinniburgh (Cavendish Laboratory, Cambridge) described his dynamical calculations of LEED intensities for the (100) surface of NiO. D. L. Adams (U. Aarhus, Denmark) outlined the transform-devolution method for the analysis of LEED data. The multiple scattering effects and "termination-of-series" errors have generally caused workers with LEED to proceed from model calculations, as opposed to x-ray workers who have traditionally used some form of transform-devolution, such as the Patterson function. Adams argued that if the transform-devolution approach is used, the multiple scattering and "termination-of-series" effects become just another random noise component. It may be so, but the applications he illustrated were for simple and clean surfaces of Al, Cu and Ni. R. Feder (Institut für Festkörperforschung der Kernforschungsanlage, Jülich) spoke on the spin-polarized LEED from low-index surfaces of W for electron energies up to 200 eV. This phenomenon may give rise to a source of intense polarized electron beams or to a new polarization detector.

R. W. Joyner (U. Bradford, UK) reviewed the application of the electron spectroscopies, AES, UPS, and x-ray photoelectron spectroscopy (XPS) to reactions on metallic surfaces. He explained the region of applicability of each of the three, presented some of the textbook examples, and even mentioned some of the folklore of the subject. H. Lüth (Technischen Hochschule, Aachen) spoke on the work he did with G. W. Rubloff and W. D. Grobman at the IBM-Yorktown Heights (and supported by ONR) on chemisorption and decomposition reactions of organic molecules on clean Pd surfaces using UPS with the He I and II lines (20.2 and 40.8 eV, respectively). Only the "fingerprint" or empirical correlation approach is possible at this time in such complicated situations.

Several theoretical models were then described in the contributed papers. R. A. van Santen (Shell Research Laboratories, Amsterdam) spoke on the chemisorption on transition metal clusters. In this report, which was much the same as that presented by van Santen at the Centre Européen de Calcul Atomique et Moléculaire planning meeting in April (see ESN 30-6:283), a complete extended



Hückel calculation is done for a finite cluster of ten or less metallic atoms with and without an adsorbed atom, usually hydrogen, to determine the binding energy. In this work he has made a study of the effects of cluster size, alloy clusters, and the adsorbed atom location. S. Holloway (Leicester University) presented calculations on the rate of desorption which showed that the gas-interface potential should be recoverable from the desorption data. A Morse potential is assumed. H. Hjelmberg (Chalmers University of Technology, Sweden) reported on theoretical work on chemisorption on a simple (i.e., jellium) metal.

G. Ehrlich (U. Illinois) gave a very colorful account of his work on the field ion microscopy of a W tip. By double exposure, one in red and the next in green, it was possible to observe directly the field-induced evaporation of a W surface atom. This has led to the development of the field desorption microscope. He then illustrated monomers, dimers and trimers in motion on the surface. These data allow a direct calculation of the surface diffusion and the dissociation rate.

Following Ehrlich, another beautifully direct experimental program was described. R. Butz (Institut für Grenzflächenforschung und Vakuumphysik, Jülich) reported on a determination of the surface diffusion coefficient by a direct measurement of concentration profiles by a direct measurement of concentration profiles and the application of the method of oxygen diffusion on the W(110) surface in the temperature range of 760 to 880°C for coverages up to one monolayer. The technique is to lay down a given coverage on one half-plane of the surface at a low temperature, producing a step profile. Then, after a prescribed thermal cycle, the contact potential difference (CPD) is measured locally, with a resolution of about 50  $\mu\text{m}$ , by a 6- $\mu\text{m}$ -dia. vibrating-wire maintained at 15  $\mu\text{m}$  above the surface. The vibrating wire is part of a voltmeter capable of measuring the CPD with a sensitivity of 20 mV. The absolute adsorbate coverages between 0.4 and 0.9 the activation energy for oxygen diffusion was found to be  $27 \pm 2$  kcal/mol and reasonably independent of the coverage. For lower coverages, the Jülich group has found a correlation between the diffusion and the oxygen adsorbate structures observed by LEED.

The final invited paper, on the scattering of low energy ions from solid surfaces, was given by A. L. Boers (U. Groningen; the Netherlands). He argued that most of the knowledge obtainable from ion scattering about the first atomic surface layers could be had by using noble gas ions with energies between 20 eV and 10 keV and detecting only the ionized particles from the surface. Experimentally this is reasonable since most ions will be neutralized if they pass to the second or third layers. For this case it is

quite accurate to assume single or multiple binary collisions, and such calculations provide a doubled-peaked energy distribution of the ions whose detailed characteristics depend on the potentials and the thermal properties of the surface layer. Though Boers thinks multiple ion scattering is a very useful tool, he admitted that other probes are needed to give the necessary information to understand the ion scattering--ion beam scattering will never in itself be a panacea of surface science.

In completing this report, I would like to mention the very useful procedure used at these International Symposia; it made the session chairmans' tasks almost a joy and must also indicate something about Dutch humor. If a speaker went over his time even one second, the lights in the auditorium would slowly dim and on a screen, next to the one for slides, would flash a Laurel & Hardy film--in Dutch--with the sound quite loud.